Enhancement of the refrigerant capacity in low level boron doped La0.8Gd0.2Fe11.4Si1.6

P Shamba
University of Wollongong, ps807@uowmail.edu.au

R Zeng
University of Wollongong, rzeng@uow.edu.au

Jianli Wang
University of Wollongong, jianli@uow.edu.au

S J. Campbell
University Of New South Wales

S X. Dou
University of Wollongong, shi@uow.edu.au

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Abstract

The effects of boron doping on the itinerant-electron metamagnetic (IEM) transition and the magnetocaloric effects (MCEs) in the cubic NaZn13-type La0.8Gd0.2Fe11.4Si1.6 compound have been investigated. The Curie temperature, TC, of La0.8Gd0.2Fe11.4Si1.6Bx compounds with x=0, 0.03, 0.06, 0.2 and 0.3 was found to increase from 200 K to 222 K with increase in boron doping, x. The maximum values of the isothermal magnetic entropy change, ΔSM, (derived using the Maxwell relation for a field change ΔB=0-5 T) in La0.8Gd0.2Fe11.4Si1.6Bx with x=0, 0.03, 0.06, 0.2 and 0.3 are 14.8, 16, 15, 7.5 and 6.6 J kg−1 K−1 respectively, with corresponding values of the refrigerant capacity, RCP of 285, 361, 346, 222 and 245 J kg−1. The large ΔSM values observed for the undoped sample, and the low level B doped La0.8Gd0.2Fe11.4Si1.6B0.03 and La0.8Gd0.2Fe11.4Si1.6B0.06 compounds are attributed to the first order nature of the IEM transition while the decrease of ΔSM at x=0.2 and 0.3 is due to a change in the second order phase transition with increase in B doping. The nature of the magnetic phase transitions is also reflected by the magnetic hysteresis of 3.7, 9, 5.7, 0.4 and 0.3 J kg−1 for x=0.0, 0.03, 0.06, 0.2 and 0.30 respectively. The possibility of tuning the TC and the magnetocaloric properties at temperatures close to room temperature make this system interesting from the points of view of both fundamental aspects as well as applications.

Keywords

8gd0, 2fe11, 4si1, 6, enhancement, capacity, refrigerant, low, level, boron, doped, la0

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Enhancement of the refrigerant capacity in low level boron doped $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$

P. Shamba[1*], R. Zeng[1], J. L. Wang[1, 2, 3], S. J. Campbell[2] and S. X. Dou[1]

[1]*Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2519, Australia*

[2]*School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia*

[3]*Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, NSW 2234, Australia*

The effects of boron doping on the itinerant-electron metamagnetic (*IEM*) transition and the magnetocaloric effects (*MCEs*) in the cubic $NaZn_{13}$-type $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$ compound have been investigated. The Curie temperature, T_C, of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with x = 0, 0.03, 0.06, 0.2 and 0.3 was found to increase from 200 K to 222 K with increase in boron doping, x. The maximum values of the isothermal magnetic entropy change, ΔS_M, (derived using the Maxwell relation for a field change $\Delta B = 0 - 5$ T) in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ with x = 0, 0.03, 0.06, 0.2 and 0.3 are 14.8, 16, 15, 7.5 and 6.6 J kg^{-1} K^{-1} respectively, with corresponding values of the refrigerant capacity, *RCP* of 285, 361, 346, 222 and 245 J kg^{-1}. The large ΔS_M value observed for the undoped sample and the low level B doped $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.03}$ and $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06}$ compounds is attributed to the first order nature of the *IEM* transition while the decrease of ΔS_M at x = 0.2 and 0.3 is due to a change to a second order phase transition with increase in B doping. The nature of the magnetic phase transitions is also reflected by the magnetic hysteresis of ~ 3.7, 9, 5.7, 0.4 and 0.3 J kg^{-1} for x = 0.0, x = 0.03, 0.06, 0.2 and 0.30 respectively. The possibility of tuning the T_C and the magnetocaloric properties at temperatures close to room temperature make this

system interesting both from the points of view of fundamental aspects as well as applications.

Keywords

Magnetocaloric; magnetic properties; doping; alloys; intermetallic compounds

1. **Introduction**

The conventional refrigeration technologies in use today based on the gas compression / expansion cooling mechanisms may gradually be replaced by the environmentally friendly and more efficient magnetic refrigeration in the near future[1-5]. The magnetic refrigeration is based on the magnetocaloric effect (MCE) which results from the coupling of a system of magnetic moments under the influence of an external magnetic field resulting in the cooling or heating of a system. An ideal material for magnetic refrigeration should be composed of cheap raw materials, have a high MCE demonstrated by a large magnetic entropy change (ΔS_M) as well as a large adiabatic temperature change (ΔT_{ad}), have minimal or no thermal/magnetic hysteresis[6,7]. The $LaFe_{11.4}Si_{1.6}$ alloy possesses all of the above mentioned characteristics and belongs to the so-called giant magnetocaloric effect (GMCE) group of materials which undergo a phase transition from one form of magnetic order to another with an associated "giant" change of entropy. With the potential for high temperature operation in mind, a drawback of this system is the relatively low ordering temperature of T_C ~195 K[8] although T_C can be tuned by introducing small atoms like B, N or C[9-11]. Introduction of the interstitial N, H, C or B atoms leads to expansion of the lattice which makes the Fe 3d band narrow and brings about the increase in T_C by reducing the Fe 3d overlap wave functions[10].

Such small atoms change the electronic structure of the compounds, which can influence the intrinsic magnetic properties of Fe-based compounds[12].

The refrigerant capacity (*RCP*) is a measure of the heat that can be transferred between the cold and hot reservoirs and, together with ΔS_M, is a key parameter for characterising the performance of magnetocaloric materials. We have therefore carried out a systematic study of the influence of boron doping on the ΔS_M and *RCP* of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds (with boron doping level, x = 0, 0.03, 0.06, 0.2 and 0. 3). It has been previously shown that the partial substitution of La with Gd enhances the $LaFe_{11.4}Si_{1.6}$ magnetocaloric properties, hence for this purpose for all our samples we substituted 20 at. % La with Gd[13]. Our results reveal that, for low boron doping levels, the magnetic field induced phase transition remains first order and causes a significant enhancement of *RCP*. However, high boron doping levels change the phase transition from first order to second order and accordingly decreases both ΔS_M and *RCP* compared to undoped $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$. We also show that for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds (with boron doping level, x = 0, 0.03, 0.06, 0.2 and 0. 3), an increase in boron doping shifts T_C towards room temperature.

2. Experimental

Ingots of polycrystalline alloys with nominal compositions $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ (x = 0, 0.03, 0.06, 0.2 and 0.3), where x is the boron doping level, were prepared by arc-melting appropriate amounts of the high purity constituent elements under a high purity argon atmosphere in a water cooled copper crucible. The purities of the starting materials were 99.9% for La, Si and Fe, 99.99% for Gd and 99.999% for B. During the arc melting process, each ingot was turned over and remelted several times to ensure its homogeneity. The total weight loss after the arc-melting procedure was less than 1 wt %, corresponding to La and Gd evaporation during the fusion, which was compensated with an La and Gd mass excess (10 at. %) to ensure the compound stoichiometry. The resulting ingots were wrapped in tantalum foil, annealed at 1323 K for 14 days in an evacuated quartz tube to improve the crystallization of the samples and then quenched in water. X - ray diffraction (XRD) measurements on powder samples were performed using Cu Kα radiation to identify the crystal structure and the crystal lattice parameter. The magnetization was measured as a function of temperature and magnetic field for the samples and was carried out using the vibration sample magnetometer (VSM) option of a quantum design 14 T Physical Property Measurement System (PPMS) in the temperature range of 150 – 300 K under applied magnetic field values up to 5 T.

3. Results and Discussion

A Rietveld plot of XRD data profile refinement with the program FULLPROF for a selected sample $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06}$ is shown in Fig. 1. The XRD indicates that the alloys crystallize well in the $NaZn_{13}$-type cubic structure with a small amount of α-Fe and LaFeSi existing as minor phases. It is imperative to note that the majority of published data on $LaFe_{13-x}Si_x$ alloys, no single-phase $LaFe_{13-x}Si_x$ alloys could be obtained[14-17]. Table 1 shows the lattice parameter, a, determined by using the Rietveld refinement as a function of the B concentration. It is clear from Table 1 that the addition of boron in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ results in a linear increase of the lattice constant from 11.464 to 11.473 for $x = 0$ to $x = 0.3$ The lattice parameters of the $NaZn_{13}$-type structure phase for the alloys increase on the addition of boron, suggesting that the boron atoms occupy interstitial sites resulting in the expansion of the lattice. The lattice expansion caused by the addition of B is shown in Table 1 and was calculated to be ~0.08 % for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$ compared to the undoped sample.

The temperature-dependent magnetization was been measured in the zero-field-cooled (ZFC) and field-cooled (FC) process for all samples in order to determine the transition temperature and the nature of the transition. The sample was first cooled in zero-field to 5 K, then a small field of 200 Oe was applied to the sample and after that the magnetization was measured in the heating process up to 300 K, thus obtaining the ZFC magnetization curve (which is not shown to enhance clarity). The FC magnetization was measured in the process of cooling sample to 5 K with the same field. Figure 2 shows the FC magnetization obtained under a magnetic field of 0.02 T for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0.3. The ferromagnetic ordering T_C of the samples is defined as the temperature at which the dM/dT of the warming M - T curves is a minimum. The T_C values for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0$ to 0.3 are found to increase linearly with increase in boron concentration to T_C = 200, 204, 205, 215 and 222 K respectively. The increase in T_C for $La(Fe,Si)_{13}$ compounds with increasing *B* concentration is consistent with results reported in literature by Xie *et al*[10]. Normally, the T_C increases as the lattice expands, or equivalently as the *Fe* - *Fe* distances increase. However, for *Fe* - rich rare - earth (*RE*) compounds, T_C depends mainly on the *Fe* - *Fe* and *Fe* – *RE* direct exchange interactions which the *Fe* - *Fe* distance strongly influences[18]. In this work the BLOKJE program was used to compute the La(8*a*) - Fe(96*i*), Fe(8*b*) - Fe(96*i*) and Fe(96*i*)-Fe(96*i*) bond lengths to help explain the increase in T_C. As expected, Table 1 shows the increase in bond length in all the above mentioned bonds with an increase in boron doping, x. Thus, the observed enhancement of T_C in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with an increase of boron doping, *x*, can be attributed to an increase in the *Fe* - *Fe* exchange interactions caused by the increasing *Fe* - *Fe* distances.

Figure 3 shows the isothermal magnetization curves of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ (with boron doping level, x = 0, 0.03, 0.06, 0.2 and 0. 3) over the temperature range 180 – 250 K which span the paramagnetic to ferromagnetic transition regions. The magnetization isotherms were measured for increasing and decreasing magnetic fields in the range ΔB = 0 – 5 T with the *PM* - *FM* transitions evident in the behaviour of all five samples. The change in the saturation magnetization is probably related to the presence of different amounts of the α-Fe in the compounds. Fig. 3 also demonstrates hysteresis for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$, $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.03}$ and $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06}$ samples compared with the insignificant hysteresis in the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.2}$ and $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$ samples. These hysteretic effects confirm the first-order nature of the magnetic transitions for the x = 0.0, 0.03 and 0.06 samples while the behaviour of the x = 0.2 and 0.3 samples is typical of a second order magnetic transition. The isothermal magnetisation curves exhibit typical ferromagnetic behaviour for all samples below their respective magnetic ordering temperatures. The $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with boron doping level, x = 0 , 0.03 and 0.06 show S - shaped magnetization curves typical for the itinerant electro-metamagnetism[12] while the magnetization curves for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$ are characteristic of a second order transition. These results are confirmed by the Arrott plots in Fig 4. The Arrott plots were used to determine the type of phase transition of the sample near T_C according to the Inoue-Shimizu model[19]. In this model, the free energy (F) of a magnetic system is expressed by the Landau expansion in powers of magnetization, M shown in Equation (1) below:

$$F(M,T) = \frac{1}{2}c_1(T)M^2 + \frac{1}{4}c_3(T)M^4 + \frac{1}{6}c_5(T)M^6 - MH \quad (1)$$

The type of transition is related to the sign of the Landau coefficient c_3 (T) at the Curie temperature (c_3 (T_C)). If c_3 (T_C) is negative, the transition is first order, otherwise the transition will be second order. The sign of c_3 (T_C) can be obtained from the Arrott plots. If there are S - shaped curves near T_C in the Arrott plots, c_3 (T_C) is negative, otherwise, it is positive. As seen in Fig. 4, the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples (with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0. 3) near their respective T_C exhibit S - shaped curves with negative slopes. The negative slopes and inflection points in these three samples confirms the occurrence of metamagnetic transitions from FM to PM state above T_C, indicating that both compounds undergo a first-order transition. This therefore means that for the low level boron doping, the B atoms do not significantly influence the shape of the density of states around the Fermi level and a strong *IEM* behaviour is still retained. However, the absence of S - shaped curves with negative slope or an inflection point in the Arrott plot for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.2}$ and $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$ (but rather an almost linear behaviour of the Arrott plot), confirms the occurrence of a second-order transition in these samples.

It has been shown recently that the magnetic entropy change (ΔS_M) of materials with hysteretic first order transitions should be calculated carefully using the Maxwell relation as the value of ΔS_M calculated from the increasing field differs from that calculated using the decreasing field[20]. The ΔS_M calculated using the increasing field has been shown to exhibit an erroneous spike, whilst the ΔS_M calculated using the decreasing field consists of a much reduced spike with a plateau[20]. Hence, for this reason, in this work we calculated ΔS_M using the decreasing field. Thus, the magnetic entropy change (ΔS_M) was calculated from the isothermal magnetization curves close to T_C using the Maxwell relation shown in Equation (2) below:

$$-\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (2)$$

Figure 5 shows the 3D plots of magnetic entropy change as a function of temperature and magnetic field, H for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with boron doping level, x = 0, 0.03, 0.06, 0.2 and 0.3. Similar to what Demuner *et al.* observed, the ΔS_M curves for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with x = 0 and 0.03 have asymmetric peaks near T_C which is attributed to the field induced metamagnetic transition above T_C with the maximum magnetic entropy changes being 14.8 and 16 J kg $^{-1}$K^{-1} respectively[13]. However, a further increase in the boron doping (x = 0.03, 0.06, 0.2 and 0.3) significantly broadens the ΔS_M versus T curve and in the case for the samples with x = 0.2 and 0.3, reducing the maximum magnetic entropy change to 7.5 and 6.6 J kg $^{-1}$K^{-1} respectively. This reduction in the magnetocaloric properties is explained by the fact that the increase of B content in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ drives the *FM – PM* transition towards second order and eliminates the meta-magnetic transition. Also, the introduction of boron atoms leads to an increase of T_C, which results in the shift of ΔS_M peaks towards higher temperatures. Thus for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds, optimum boron doping occurs at low levels since the lowly boron doped sample (x = 0.03) exhibits the highest magnetic entropy change.

In order to assess the usefulness of the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ alloys as magnetic refrigerant materials, the *RCP* is calculated according to equation (3) below:

$$RCP = -\Delta S_M \times \partial T_{FWHM} \tag{3}$$

where ∂T_{FWHM} is the width at half maximum obtained from the temperatures at half the maximum peak value of the ΔS_M versus T curve. The calculated results of *RCP* for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with boron level, x = 0, 0.03, 0.06, 0.2 and 0. 3 plotted as a function of the magnetic field are shown in Fig. 6. For all the samples, the maximum values of *RCP* are found to increase with an increase in the applied magnetic field and reach the values of 285, 361, 346, 222 and 245 J kg^{-1} for the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with boron level, x = 0, 0.03, 0.06, 0.2 and 0. 3 respectively under a field change of 0 – 5 T. This figure, clearly illustrates the fact that the lowly doped sample (x = 0.03 and 0.06) exhibit significantly higher *RCP* compared to the undoped sample, whilst the highly doped samples (x = 0.2 and 0.3) exhibit significantly lower *RCP* values as compared to the undoped sample.

Table 1 shows the hysteresis loss, defined as the area enclosed by the ascending and descending branches of the magnetization curve. The maximal hysteresis losses around T_C for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with boron level, x = 0, 0.03, 0.06, 0.2 and 0. 3 are 3.7, 9.1, 5.7, 0.4 and 0.3 J kg^{-1} measured under a 5 T field respectively. This reduction in hysteresis losses at high boron doping levels (i.e, x = 0.2 and 0.3) is attributed to the weakening of the field induced first order magnetic transition (FOMT) from the paramagnetic to the ferromagnetic state due to the addition of boron. By subtracting the hysteresis loss from the calculated RCP, we obtained the effective refrigerant capacity, RC_{eff} which is also shown in Table 1, calculated for magnetic field values of 5 T. As boron doping, x varies from 0 to 0.3, the RC_{eff} shows a similar trend to that observed in the RCP. These results indicate that the introduction of interstitial boron atoms significantly improves the cooling capacity of the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ material system at all values of the applied magnetic field, *H*

Clearly of the five samples investigated, $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.03}$ is the preferred magnetic refrigerant material as it would support the transport of the greatest amount of heat in a practical refrigerator. Therefore, low level boron doping enhances the *MCE* in the $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ material system.

Table 2 shows a summary of the present results, as well as the *MCE* properties of La_{1-}

$_x$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds with Gd and LaFe$_{11.4}$Si$_{1.6}$ included for comparison. The inconsistency of the reported *MCE* properties is apparent even for compounds with the same composition and is discussed in detail below. Investigation of La substitution by the rare-earth element Gd was first reported in 2007 by Passamani *et al*. They found that for 5 at. % La substituted by Gd, the first order transition is destroyed leading to a drastic reduction of its maximum magnetic entropy change[8]. This seems to be in disagreement with the work of Demuner *et al*. (2009) which shows that for 5 at. % La substituted by Gd, the magnetic transition remains first order and the maximum magnetic entropy change remains relatively high[13]. In 2008, Kumar *et al.* investigated the *MCE* properties of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$. This group observed a drastic reduction in the maximum magnetic entropy change of the above mentioned compound with the first order transition being destroyed[21]. Thus, the discrepancies in the *MCE* properties of La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds studied by the several groups mentioned above can be attributed to the presence of different impurities in samples with the same composition thereby influencing the *MCE* properties. Also, it has been previously established that the T_C of Si based compounds is strongly dependent on the *Si* content in the NaZn$_{13}$-type structure, hence the discrepancy in the T_C of the La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds in Table 2 can be attributed to the different Si content in the actual compositions of the compounds even though they may have the same Si content in the nominal compositions[22, 23].

Our investigation reveals that for 20 at. % La substituted by Gd, the maximum magnetic entropy change remains relatively high (compared to LaFe$_{11.4}$Si$_{1.6}$) whilst the magnetic transition remains first order, which is in contrast to Kumar *et al.* (2008). We then studied the influence of boron doping on La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and our results show that at low boron doping levels (x = 0.03 and 0.06), the T_C, ΔS_M and *RCP* are all significantly enhanced, whilst the magnetic transition remains first order. However, at high boron doping levels ($x = 0.2$ and 0.3), T_C increases whilst both ΔS_M and *RCP* are significantly reduced with the first transition order being destroyed. MCE changes due to interstitial or substitutional modifications are common in $La(Fe,Si)_{13}$-based compounds due to the fact that the magnetic properties of these compounds are dominated by the characteristics of the Fe 3d electron band structures. Therefore, the variation of T_C in these compounds is mainly associated with the lattice constant in keeping the characteristic band structure. As reported in the Ref 24, the hydrogen atoms in the interstitial positions expand the lattice parameter and in so doing, changes the magnetic properties. So the interstitial atoms play two roles on modifying the magnetic properties: (1) expanding the lattice parameter and (2) varying the chemical environments. However, in the present case, unless we perform the external pressure experiment, it is difficult to separate these roles.

4. Conclusions

We have investigated the effect of boron doping on the magnetic and magnetocaloric properties of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds (with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0. 3). We have shown that the paramagnetic to ferromagnetic transition in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds, which is first-order for $x = 0$, 0.03 and 0.06 can be tuned to second-order at high boron doping levels ($x = 0.2$ and 0.3). A considerable enhancement of T_C, ΔS_M and *RCP* was observed at low boron doping levels ($x = 0.03$ and 0.06). Thus, at low boron doping levels, the enhancement of *MCE* in $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ alloys makes this material system a promising candidate for magnetic refrigeration near room temperature.

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Figure Captions:

Table 1: Magnetic hysteresis loss, lattice parameter, RC_{eff} and bond angles of $La_{1-x}Gd_xFe_{11.4}Si_{1.6}$ compounds, measured at 5 T

Sample	Loss (J/kg)	RC_{eff} (J/kg)	a(Å)	Bond Lengths (Å)		
				La(8a)-Fe(96i)	Fe(8b)-Fe(96i)	Fe(96i)-Fe(96i)
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$	3.7	281	11.4637(4)	3.3468(7)	2.4519(2)	2.8292(8)
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.03}$	9.1	352	11.4641(8)	3.3470(2)	2.4520(3)	2.8294(1)
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06}$	5.7	341	11.4646(2)	3.3471(4)	2.4521(1)	2.8295(1)
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.2}$	0.4	226	11.4649(9)	3.3472(5)	2.4522	2.8296(1)
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$	0.3	249	11.4728(6)	3.3495(6)	2.4538(9)	2.8315(5)

Table 2: Discrepancies in the reported *MCE* properties of $La_{1-x}Gd_xFe_{11.4}Si_{1.6}$ compounds, measured at 5 T.

Sample	Order of transition	T_C (K)	$-\Delta S_M$ (J kg $^{-1}$K^{-1})	RCP (J kg $^{-1}$)	Ref
*Gd	2nd	294	10.2	410	22
*$LaFe_{11.4}Si_{1.6}$	1st	195	18	324	8
$La_{0.95}Gd_{0.05}Fe_{11.4}Si_{1.6}$	2nd	215	7	210	8
$La_{0.95}Gd_{0.05}Fe_{11.4}Si_{1.6}$	1st	~210	~15	-	13
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$	2nd	215	7.9	-	21
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}$	1st	200	14.8	285	This work
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.03}$	1st	204	16	361	This work
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06}$	1st	205	15	346	This work
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.2}$	2nd	215	7.5	222	This work
$La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$	2nd	222	6.6	245	This work

*These samples are shown for the purpose of comparison

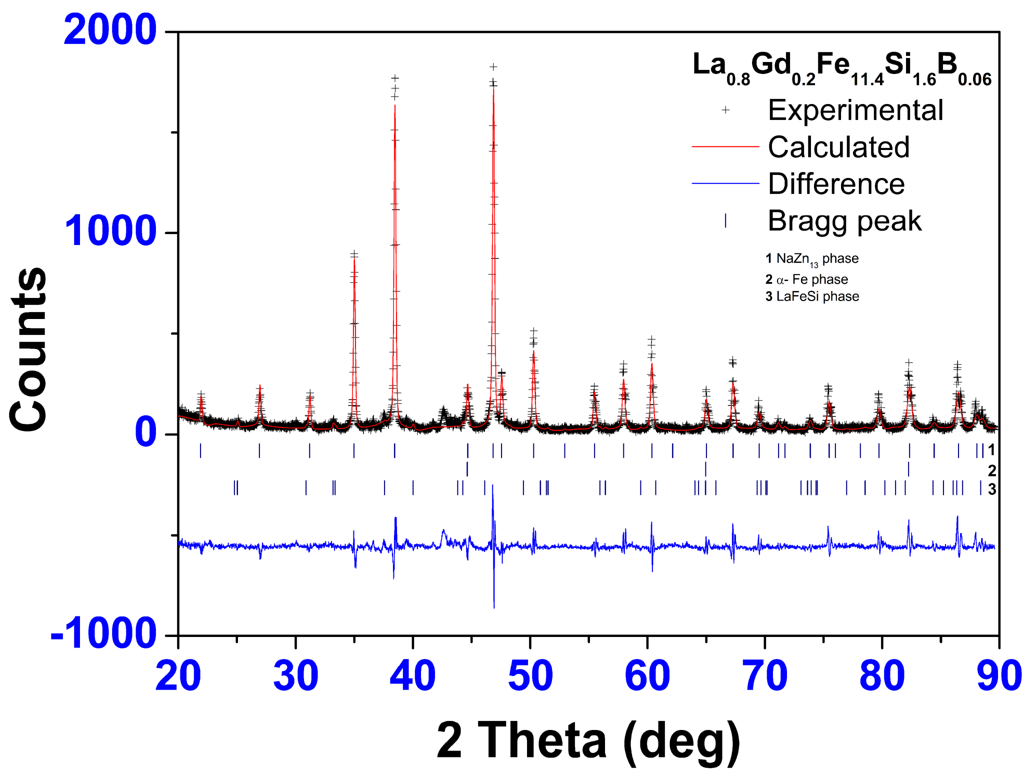

Fig 1: Rietveld plot of XRD data for a selected sample, $x = 0.06$ at 300 K.

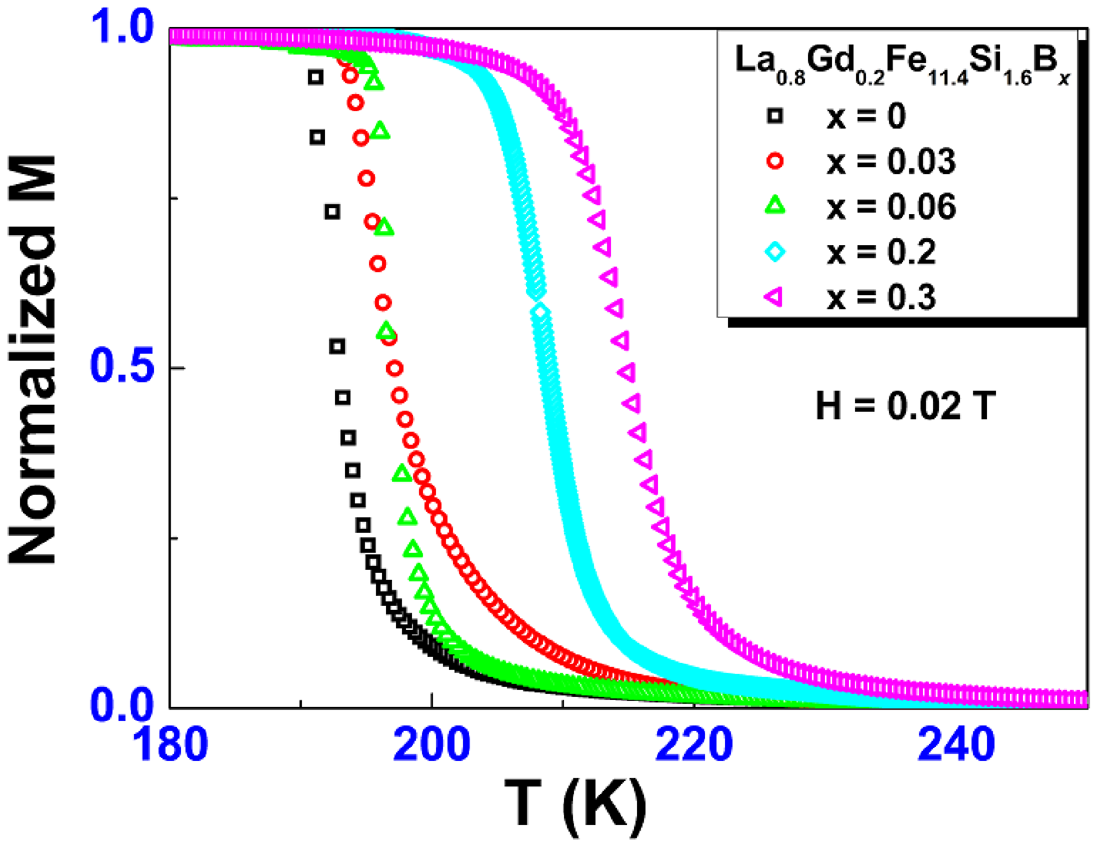

Fig. 2: Thermomagnetization curves of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds (with boron doping level, x = 0, 0.03, 0.06, 0.2, 0.3). The samples were measured on warming in a magnetic field of B = 0.02 T after first cooling to 100 K in zero field.

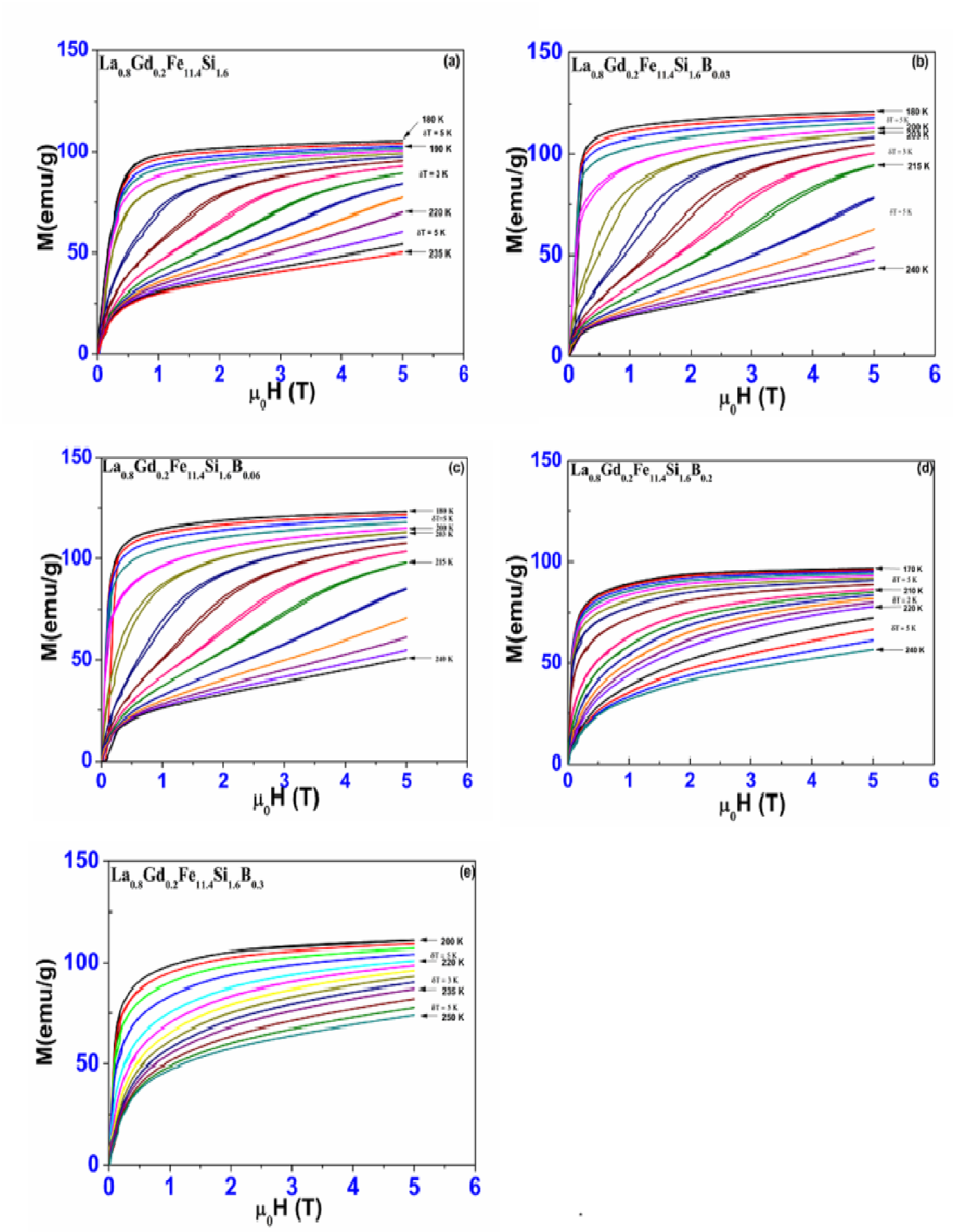

Fig. 3: Magnetization isotherms of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with boron doping level, $x = 0, 0.03, 0.06, 0.2, 0.3$ measured in the field ascending and the field descending processes in a range of temperatures around T_C.

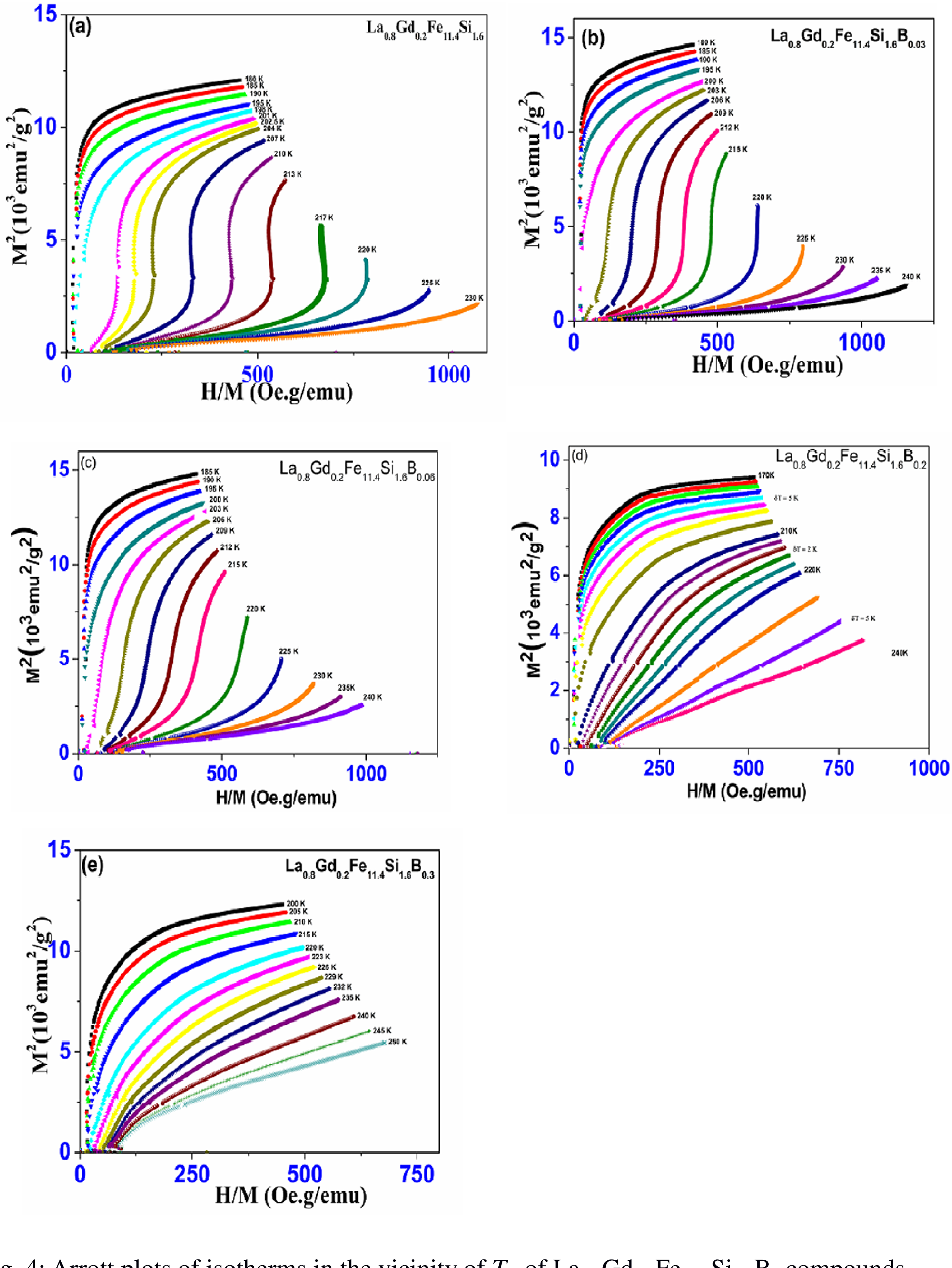

Fig. 4: Arrott plots of isotherms in the vicinity of T_C of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with boron doping level, $x = 0, 0.03, 0.06, 0.2, 0.3$.

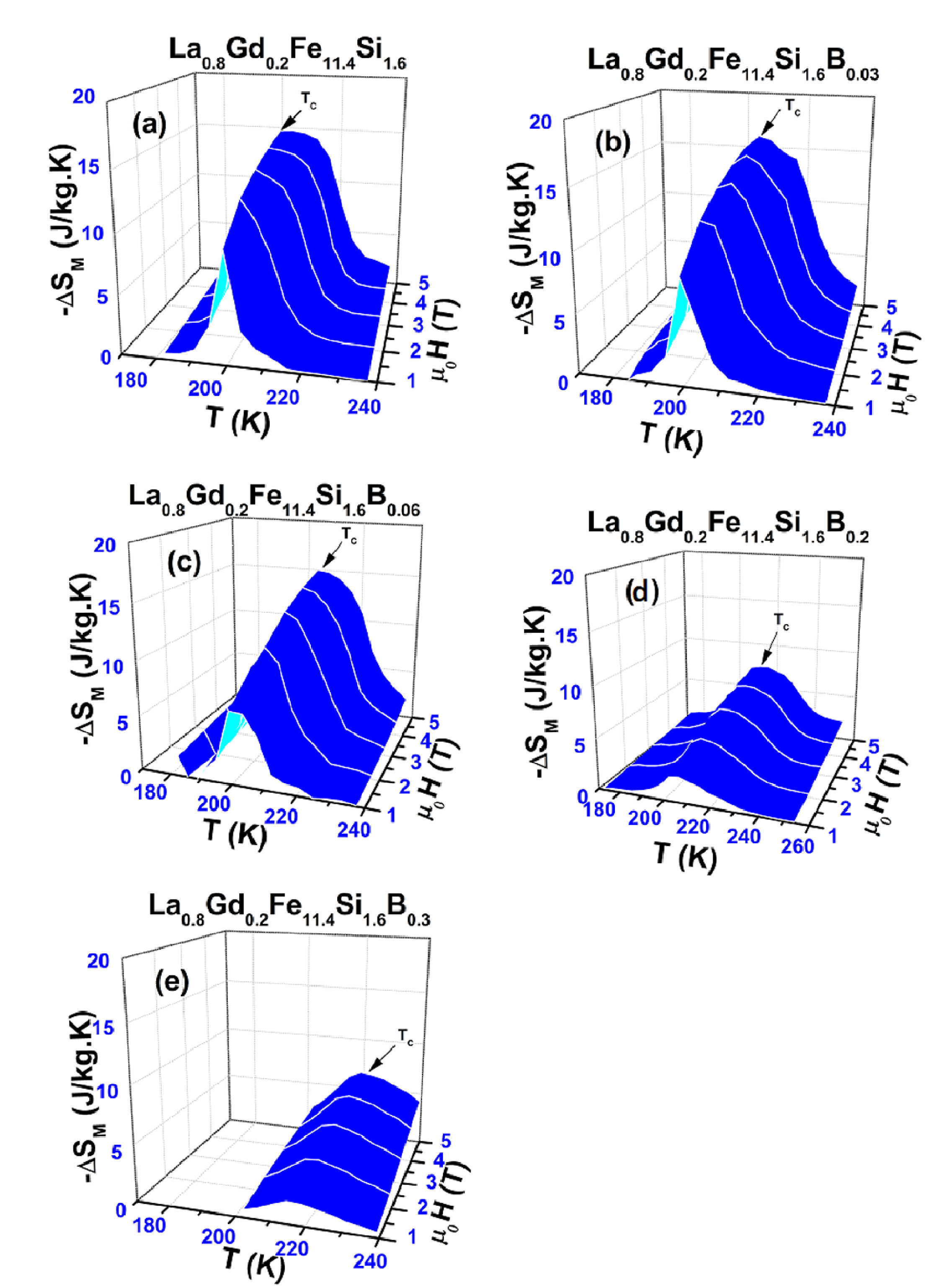

Fig. 5: Temperature and magnetic field dependence of the isothermal magnetic entropy change of $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with boron doping level, x = 0, 0.03, 0.06, 0.2, 0.3 measured at 5 T calculated from the Maxwell relation.

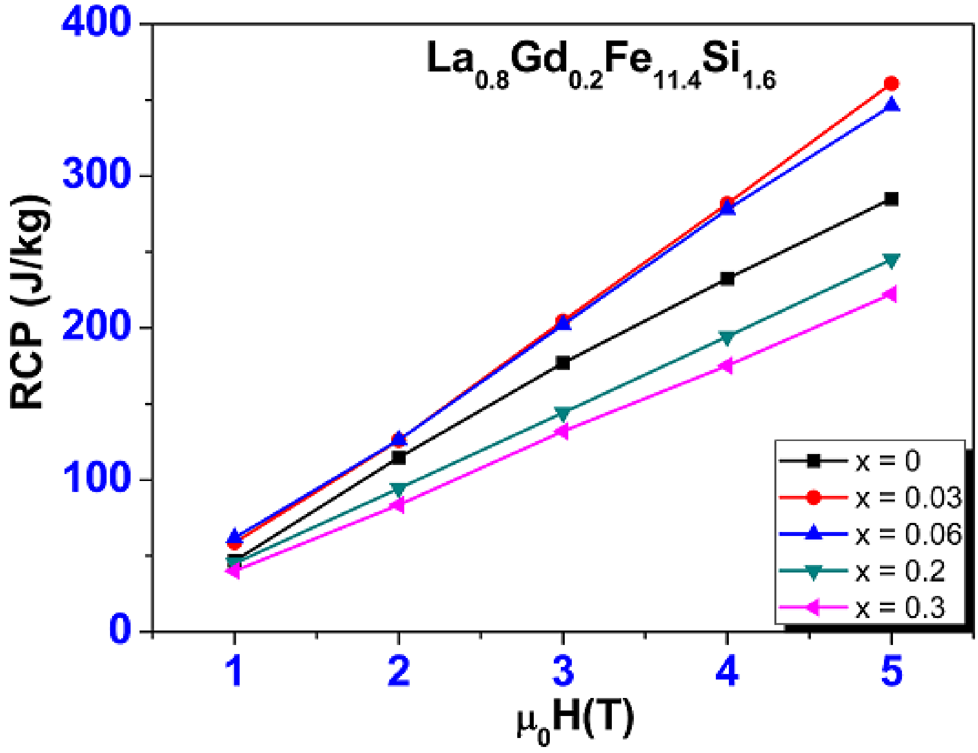

Fig. 6: Field dependences of the refrigerant capacity for $La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds with boron doping level, x = 0, 0.03, 0.06, 0.2 and 0.3 measured at 5 T.